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Chromium isotopic homogeneity between the Moon, the Earth, and enstatite chondrites

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ABSTRACT

Among the elements exhibiting non-mass dependent isotopic variations in meteorites, chromium (Cr) has been central in arguing for an isotopic homogeneity between the Earth and the Moon, thus questioning physical models of Moon formation. However, the Cr isotopic composition of the Moon relies on two samples only, which define an average value that is slightly different from the terrestrial standard. Here, by determining the Cr isotopic composition of 17 lunar, 9 terrestrial and 5 enstatite chondrite samples, we re-assess the isotopic similarity between these different planetary bodies, and provide the first robust estimate for the Moon. In average, terrestrial and enstatite samples show similar ε^{54}Cr. On the other hand, lunar samples show variables excesses of ^{53}Cr and ^{54}Cr compared to terrestrial and enstatite chondrites samples with correlated ε^{53}Cr and ε^{54}Cr (per 10,000 deviation of the ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr ratios normalized to the ^{50}Cr/^{52}Cr ratio from the NIST SRM 3112a Cr standard). Unlike previous suggestions, we show for the first time that cosmic irradiation can affect significantly the Cr isotopic composition of lunar materials. Moreover, we also suggest that rather than spallation reactions, neutron capture effects are the dominant process controlling the Cr isotope composition of lunar igneous rocks. This is supported by the correlation between ε^{53}Cr and ε^{54}Cr, and ^{150}Sm/^{152}Sm ratios. After correction of these effects, the average ε^{54}Cr of the Moon is indistinguishable from the terrestrial and enstatite chondrite materials reinforcing the idea of an Earth–Moon–enstatite chondrite system homogeneity. This is compatible with the most recent scenarios of Moon formation suggesting an efficient physical homogenization after a high-energy impact on a fast spinning Earth, and/or with an impactor originating from the same reservoir in the inner proto-planetary disk as the Earth and enstatite chondrites and having similar composition.

1. Introduction

The mechanism at the origin of the Earth–Moon system that is the most consistent with chemical and physical observations is through a giant impact(s) with the proto-Earth (Canup, 2004; Canup, 2012; Ćuk and Stewart, 2012; Ćuk et al., 2016). Canonical numerical simulations predicted that significant amount of the impactor should reside in the Moon, and thus that it could be detected in lunar samples. However, elements that display large nucleosynthetic anomalies between solar system materials (e.g., O, Ti, Cr) are isotopically similar in terrestrial and lunar samples (e.g. Qin et al., 2010; Zhang et al., 2012; Young et al., 2016), therefore questioning canonical models of Moon's formation suggesting that most of the Moon was composed of impactor materials (Canup, 2004). The first scenario that has been suggested to reconcile geochemical observations and canonical numerical simulations was the post-impact isotopic homogenization between the proto-Earth and the Moon through silicate vapor exchange (Pahlevan and Stevenson, 2007). However, while isotopic equilibrium can be achieved this way for volatile elements like O during the cooling timescale in the aftermath of the impact, it is almost impossible for the most refractory elements such as Ti (Tc = 1582 K, with Tc the 50% condensation temperature), Fe (Tc = 1334 K), Cr (Tc = 1296 K) (e.g. Lodders, 2003; Zhang et al., 2012; Sossi and Moynier, 2017). Based on the Ti isotopic similarity between the Earth and the Moon, it was therefore proposed that the Moon consists almost exclusively of terrestrial material (Zhang et al., 2012) unlike what is predicted by the canonical impact model. Alternatively, more recent studies also proposed that the Moon-forming impactor had an isotopic composition very close to that of the proto-Earth, and the only group of meteorites with a similar isotopic composition,

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the enstatite chondrites (e.g. Jacobsen et al., 2013; Dauphas et al., 2014a, 2014b). In order to account for the isotopic similarities between the Earth–Moon system and enstatite chondrites (EC), it has been suggested that these materials initially came from the same uniform reservoir located in the inner part ($\leq$1.5 AU) of the protoplanetary disk, and only lately diverged in their chemical evolution (e.g. Jacobsen et al., 2013; Dauphas et al., 2014a, 2014b). This hypothesis would be consistent with both geochemical observations and state of the art of numerical simulations. However, a new set of numerical calculations that are based on a fast spinning Earth and a high energy impact (Ćuk and Stewart, 2012; Lock et al., 2016; Ćuk et al., 2016) have opened up again the possibility of a high degree of post impact isotopic homogenization between the Earth and the Moon, through the direct condensation of the Moon from an already well-mixed bulk silicate Earth vapor disk (Lock et al., 2016). In this model, this type of high energy impact leaves a system in a specific state where the Earth's vaporised mantle and the disk forms a homogeneous medium from which the Moon grows and equilibrates. This scenario could also account for the isotopic similarity observed between the Earth and the Moon.

Recently, small mass-independent O isotopic offsets between the Earth and the Moon have been reported and interpreted as evidence for the detection of the impactor (Herwartz et al., 2014), however, these results have subsequently been questioned (Young et al., 2016). Furthermore, although the Cr isotope compositions (expressed as per 10,000 deviation of the ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr ratios normalized from the NIST SRM 3112a standard) have been used as an argument in favor of the Earth–Moon system homogeneity, the limited dataset available for the Moon indicates a small isotopic difference between the two planetary objects (Qin et al., 2010; Warren, 2011). The Moon shows a slightly higher ε^{54}Cr (i.e. sample 12061: $\varepsilon^{54}\text{Cr} = 0.22 \pm 0.10$, Qin et al., 2010) compared to the terrestrial standard, and enstatite chondrites ($\varepsilon^{54}\text{Cr} = 0.02 \pm 0.11$, 2sd, $n = 10$, Trinquier et al., 2007; Qin et al., 2010). This could either be interpreted as an indicator for the nature of impactor, or it may be caused by the modification of the initial Cr isotopic composition through secondary processes. However, this average composition is based on the analysis of two lunar basalts only (Qin et al., 2010), and therefore it does not represent a robust estimate of the lunar Cr isotopic composition. Furthermore, the number of Cr isotopic measurements of terrestrial materials is relatively scarce (Trinquier et al., 2007; Qin et al., 2010), and all samples seem systematically slightly enriched in ^{54}Cr ($\varepsilon^{54}\text{Cr} = 0.00 \pm 0.08$ to 0.20 ± 0.15, $n = 8$) compared to the terrestrial standard (NIST SRM 3112), as previously observed for Ni (e.g. Elliot and Steele, 2017) and Sr (Moynier et al., 2012). In order to evaluate if a possible isotopic difference between the Earth and the Moon does really exist, we investigate for the first time a much broader set of lunar samples ($n = 17$) from various geological settings (mare basalts, ferroan anorthosites, Mg-suite, regoliths) and Apollo missions (12, 15, 16 and 17) together with nine terrestrial samples including basalts and peridotites and five enstatite chondrites.

2. Samples and methods

2.1. Analytical procedure

All chemical separations and isotopic measurements were performed at the Institut de Physique du Globe de Paris, France. Dozens to hundreds of mg of bulk rock samples were dissolved in an adjusted volume of concentrated HF and HNO_3 mixture (ratio 3:1) in Teflon bombs at 140 °C for several days until complete dissolution, including multiple ultrasonication steps. No residual gels and/or refractory phases were observed during the final inspection of the solution. This dissolution procedure has previously been tested with success on pure chromite grains (Göpel et al., 2015). From these dissolutions, aliquots (equivalent to a mass $\leq$100 mg) were pipetted in order to target about 10 µg of Cr after separation on a single column. The chemical procedure adopted from Trinquier et al. (2008) includes 3 separation steps of Cr on cationic exchange resin AG50W-X8, and allows a $\geq$99% yield. ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr isotope ratios were measured by using a Fisher Scientific multi-collection (9 cups) Thermal-Ionization Mass-Spectrometry (TIMS) Triton. The details of the Cr isotopic measurements were published by Göpel et al. (2015). A purified Cr fraction, corresponding to 1–2 µg, was loaded in chloride form on degassed W filaments together with an Al–silica gel–H_3BO_3 emitter in order to facilitate Cr emission and stability. A typical measurement comprises 20 blocks of 10 cycles. Each single run (indicated as the letter n in Table 1) represents a combination of 3 successive multi-collection measurements with ^{53}Cr, ^{52}Cr and ^{54}Cr isotopes in the center cup. The isotopic ratios obtained with each configuration represent independent measurements that can be averaged, compared to each other, and used to control the evolution of the instrument over time. ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr ratios of each beam configuration were normalized using an exponential law to $^{52}\text{Cr}/^{50}\text{Cr} = 19.28323$ (Shields et al., 1966). The ^{56}Fe intensity was monitored in order to control a possible isobaric interference of ^{54}Fe with ^{54}Cr. All samples were loaded at least two times on filaments. Chemistry and measurements have been duplicated for lunar sample 15555, and give similar isotopic value (Table 1). Our data for enstatite chondrites and terrestrial rock standard BHVO-2 are consistent with earlier work (Trinquier et al., 2007; Qin et al., 2010) (Fig. 1). Final Cr isotopic data are given in ε-units that represent the relative deviation in parts per 10,000 of ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr ratios normalized to a terrestrial standard (NIST SRM 3112a Cr standard). All uncertainties are 2 standard errors (2 s.e.).

2.2. Samples overview

The chromium isotopic compositions of 17 lunar samples from Apollo 12, 14, 15, 16 and 17 missions (samples allocated by the CAPTEM committee) have been analyzed: 5 basalts (12002, 12005, 12040, 12063, 15555), 4 anorthosites (60015, 62255, 65315, 67955), one norite (77215), one dunite (72415), and 6 regolith samples (14163, 15041, 60501, 64501, 65701, 78221).

The basalts contain chromites mostly found as inclusions in pyroxenes and olivines, less frequently in the mesostasis (El Goresy et al., 1971). Samples 12005 and 12063 also show evidence for micrometeorite craters at their surface (Bloch, 1971). Anorthosites are cataclastic breccias but they have conserved pristine elemental compositions (Warren and Wasson, 1977). They exhibit systematically younger ($\leq$50 My) exposure ages than basalts (90–300 My). Although some of them show traces of micro-impacts, their meteoritic siderophile elements content is low. Sample 62255 is atypical because it contains a very large amount of impact melt ($\geq$35%; Ryder and Norman, 1980). The regolith represents admixtures of various components (fused material, plagioclase, mafic clasts, glass, highland and mare lithics) with different degrees of maturity; the average size of the grains ranges from 43 µm (78220) up to 100 µm (64501), and Is/FeO index (Is: relative concentration of nanophase metallic iron with ferromagnetic resonance) is between 55 (14163) and 110 (65701). Five enstatite chondrites including 3 EH (Qingzhen, Abee, Kota-Kota) and 2 EL (The Eagle, MAC88184) types were also studied. Finally, 9 terrestrial samples including basaltic references (BHVO-2, BE-N, NIST688), an East Pacific Rise basalt (10PUB22-07), and basalts from Cape Verde (CV-SN-98-19) and the Azores (KBD408729), as well as 2 peridotites from the Balmuccia massif (BM23, BM26) and one from the Kola